Continuous Purification of Trivalent Chromium Plating Baths

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Introduction:

The U.S. EPA has mandated waste minimization as a driving force for American industry.[1] The metal finishing industry has felt the impact of waste minimization strongly.

There are three obvious ways to implement waste minimization: The first, good operating practices, involves proper rinsing procedures, bath selection (such as the replacement of hexavalent chromium with trivalent chromium), and a company's specialization on a few processes rather than attempts to serve every possible customer in the country. Institution of good practices generally involves limited cost and significant advantages.

The second waste minimization procedure is waste recovery and reuse. This technique has been proven by companies such as Bio-Recovery Systems (BRS) and can often come very close to the ideal of "zero discharge." The combination of waste recovery with good operating practices is a very powerful asset for a company trying to achieve EPA's waste minimization mandates.

The third method of waste minimization is rarely practiced in this country, probably because it requires access to a high level of technology (except for hexavalent chromium purification which is relatively easy). This method involves purification of plating baths to avoid their being discarded. It is bath purification that I wish to discuss today.

Bath Purification

The use of plating baths causes contaminants to build up. These contaminants eventually make the plating bath unusable. For trivalent chromium baths, deterioration in bath performance appears when the impurity concentration reaches a certain level. When this happens, the trivalent chromium bath must be chemically purified and/or dummied and in cases of extreme contamination, discarded.

Ideally, the bath could be purified by a simple, safe method to allow its continued use. Several methods have been developed to remove these contaminants to allow for the continued productive use of the bath. Among the major ones are:

1.   Chemical precipitation.   This method is used to purify several plating baths including trivalent chromium baths. Unfortunately, there can be costly bath down-time when this process is used and the precipitate can be difficult to filter.   In addition, the cost of the precipitating chemical and the cost of disposing of the waste precipitate must be considered.   Finally, since this is a batch process, the impurity levels increase during bath use, then decrease during precipitation.   This results in impurity levels which follow a sawtooth shaped curve and may cause variability in plating results.

2.   Dummying.   This process involves plating impurities onto a dummy electrode.   For purification of trivalent chromium baths, copper, lead, and zinc are easily removed by dummying, but nickel is not.   Like chemical precipitation, dummying is a batch process, so the impurity levels increase during bath use, then decrease during the purification step.   This results in impurity levels which follow a sawtooth shaped curve and may cause variability in plating results. Dummying also consumes some bath constituents that must then be replenished by the plater.

3.   Electrodialysis.   This method uses membranes and an electric current to purify plating baths.   The best example is the purification of hexavalent chromium baths.   Unfortunately, electrodialysis will have limited applications because it is unable to separate cationic materials selectively.   The concept of selectivity will be discussed later.

4.   Conventional Ion Exchange.   Ion exchange has been used for the purification of hexavalent chromium plating baths for at least 30 years.   This technique, however, involves conventional non-selective ion exchange resins and will suffer from the same limitations as electrodialysis.   Still, there are some applications where conventional ion exchange can be used and BRS is familiar with these.

5.   Selective ion exchange.   With the development of ion exchange media that are capable of showing a much higher affinity for one ion than another, the ability to use ion exchange for bath purification has been greatly enhanced.   Unfortunately, there is no resin that is completely specific for one metal to the exclusion of all others,[2] but careful selection of resins allows BRS to achieve remarkable levels of selectivity.   The concept of selectivity will be discussed further below.

The use of selective ion exchange allows for very economical bath purification, consistently low impurity levels, and continuous uniformity in bath operations. No other method offers these advantages.

Ion Exchange

A brief discussion of ion exchange technology will be helpful. The first misconception that must be removed is that ion exchange is a simple process. While it is easy to conceptualize this process, and while BRS has improved the technology to the point that it is easy for customers to use ion exchange systems, the design and construction of systems is subject to a very long learning curve and is best practiced by one skilled in the art. For example, it is critical to consider many issues in designing a system. BRS has greatly expanded the scope of ion exchange into heavy metal recovery by giving careful consideration to: stream segregation, pH, hydraulic considerations, regeneration schemes, and demand based regeneration through the use of metal ion detectors.[3] Even resin selection is not trivial since there are about 2000 different ion exchange resins available in the world today (most of these are available in the U.S.) and more than two dozen selective ion exchange resins.[4]

One major consideration in selecting an ion exchange resin for a given application is the resin's *selectivity*. This is simply a description of a resin's relative affinity for a given ion *under a given set of conditions*. Typically, the selectivity is represented as a relative value such as the selectivity of a typical amino-diacetate resin:

$$Fe^{3+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Fe^{2+} > Ca^{2+} > Na^+$$
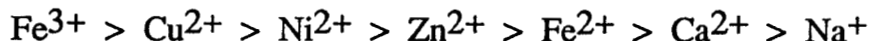
It is important to realize that the selectivity can change dramatically depending on pH, relative metal ion concentrations, and which anions are present. This is why a feasibility test should be performed to find the best resin for a given application. Theoretical considerations are not sufficient.

In deionization or softening of water, selectivity does not generally have a major impact on resin performance. Selectivity is critical in the case of bath purification, where, for trivalent chromium

purification, one needs to remove a few tens of parts per million of nickel, copper, and zinc from several thousand parts per million of trivalent chromium.

Another important criterion for ion exchange media is the resin's capacity for metals. Generally, higher capacity is better. It is important to realize that the capacity figure given by the ion exchange manufacturer, the total (or theoretical) capacity, is generally useless in determining the performance of a selective ion exchange system. The important figure is the operating capacity that can only be determined by experiment and which may only be a small fraction of the theoretical capacity. Figure 1 shows a standard breakthrough curve that shows the operating performance of an ion exchange system. The vertical axis shows the level of the ion of interest in the ion exchange effluent at a given time. The horizontal axis is a measure of how much liquid has been treated (usually expressed in bed volumes). If an ion exchange resin is run for a long enough time, the effluent concentration of all ionic species will equal the influent concentrations. The resin is said to be saturated at this point. Generally, the resin is regenerated much earlier--when breakthrough occurs. Breakthrough is the point at which metal ion levels begin to increase rapidly.

For reasons already discussed, trivalent chromium purification is an especially challenging application for ion exchange. The following information describes the experimental details.

Trivalent Chromium Bath Used

Engelhard trivalent chromium baths contain 22,000 ppm of trivalent chromium and several proprietary additives. The pH is about 2.8. The most common contaminants are nickel, zinc, and copper and the concentration of these contaminants depends on the composition of the parts being plated. When the total concentration of these metals exceeds about 100-200 ppm, product quality suffers. The actual upper limit depends on the relative amounts of the contaminants present.

Experimental Procedure

A sample of Engelhard Tri-Chrome® Plus was spiked with reagent grade nickel sulfate, copper sulfate, and zinc sulfate. Ion exchange columns were run at a flow rate of 100 ml per hour

through a resin bed volume of 5 ml. Samples were collected and analyzed for copper, nickel, zinc, iron, and chromium by flame atomic absorption spectroscopy. It was found that some element of the bath was enhancing the signal for several elements, so the bath was diluted 40 fold to obtain reproducible, accurate values.

Results

Many commercial and experimental resins were tested and the most interesting results are presented below.

1.   Figure 2.   AZ-206 had the best performance of the strongly acidic resins tested. As expected, the strongly acidic resin had very poor selectivity and exhibited breakthrough of both copper and nickel almost immediately.

2.   Figure 3.   AZ-505 is a widely used commercial copper selective chelating resin. As shown, the copper removal efficiency was acceptable, but the resin had insufficient capacity for nickel or zinc. This was because the selectivity for copper was adequate, but the selectivity for nickel and zinc was not.

3.   Figure 4.   AZ-506 is an experimental chelating resin which is reported to have good copper selectivity in many systems. For trivalent chromium purification, copper selectivity was adequate, but nickel and zinc selectivity was not.

4.   Figure 5.   AZ-509 is a chelating resin that has reasonable selectivity for zinc. The nickel selectivity was inadequate.

5.   Figure 6.   AZ-511 is a chelating resin with adequate selectivity for zinc and copper, but not for nickel.

6.   Figure 7.   AZ-105 is an interesting case. Although classified as a weakly acidic resin that would be expected to have little or no ability to remove metals from solution at this pH, AZ-105 has some chelating properties and was able to remove a modest amount of copper. Still, the capacity was too low to be useful.

7.   Figure 8.   AZ-507 had better performance than any other resin tested. This resin is a chelating resin specifically designed for heavy metal selectivity. Figure 8 shows that the resin's ability to remove copper, nickel, and zinc is much better than any other resin

tested. After treatment of 180 bed volumes (corresponding to a 9 hour cycle) on these heavily spiked samples, the AZ-507 resin was still not completely saturated with the contaminants. This resin was therefore selected for field testing using the BRS PETE unit for on site verification of the laboratory study.

Frequently, chelating ion exchange resins show high sensitivity to flow rates because of diffusional limitations.[5] Therefore, the experiment in Figure 8 was repeated using one half the initial flow rate. As shown in Figure 9, the results were not substantially different, so the system is not kinetically constrained.

Having demonstrated that BRS' AZ-507 can remove the impurities from the Engelhard Tri-Chrome® Plus plating bath, it was necessary to show that the resin can be regenerated to allow reuse of the resin. Figure 10 shows the regeneration data. The first nine bed volumes used Additive A as a stripping agent while the remainder of the experiment used Additive B. Based on this and other experiments, it was found that copper regeneration requires a different reagent than the other metals.

The use of Additive A as a regenerant may cause problems for some locations because the regenerant will generally be sent to the customer's waste treatment system and Additive A may temporarily reduce the efficiency of the waste treatment system. If no copper is present, Additive A may not be needed. Even when copper is present, Additive A may be needed only on a periodic basis. Further work is being done to eliminate the use of Additive A.

This laboratory process was next taken to a pilot system involving a 40 gallon trivalent chromium bath using the BRS "PETE" (Portable Effluent Test Equipment) unit. The pilot test results were essentially the same as the laboratory results.

Finally, a 500 gallon plating bath located at a commercial account was tested with the PETE unit which was loaded with AZ-507. This account operated their plating bath 20 hours per day, four or five days per week. Both nickel plated steel and brass parts were finished with Engelhard Tri-Chrome. Nickel was the major contaminant at 200 ppm. Within four days after starting the PETE unit, the nickel level was reduced to 120 ppm. The pumping rate of 0.5 gpm through the 0.25 cubic foot of resin dictated that a regeneration would be necessary each weekend during non-

production hours while other routine maintenance was performed. By the end of the fourth week, the nickel level had fallen to 35 ppm. After 8 weeks, the concentration reached 25 ppm of nickel and has remained constant since. The nickel concentration curve as a function of treatment time is shown in Figure 11. The PETE unit now serves as a "polishing" unit and operates only for a fraction of the bath's operating time. The regeneration cycle has been reduced to every second weekend. No chemical purification has been required since the beginning of the test nor has the tank been dummied.

If the customer starts the purification process with a fresh bath rather than with a contaminated bath, the size and expense of the unit can be reduced. If, on the other hand, the customer wishes to rejuvenate a contaminated bath more quickly, a larger unit could be provided.

Conclusions:

It has been shown at laboratory, pilot, and commercial scale that the use of BRS' patented AZ-507 process for removal of impurities from Engelhard's Tri-Chrome® Plus trivalent chromium baths is practical. Further work is underway to define the least expensive on-line bath purification system design for commercial application.

Trivalent chromium purification now joins the list of plating baths that can be purified by selective ion exchange. Table 1 shows some applications that have been developed, although others should be possible. BRS has applied for patents in this area.

Table 1
Plating Baths Purified by Ion Exchange:

Chromium (hexavalent)
Chromium (trivalent)
Electrogalvanizing (zinc sulfate)
Electroless nickel
Electrolytic nickel
Fluoroboric acid etch
Hydrochloric etch
Nickel strike
Phosphoric acid pickling solution
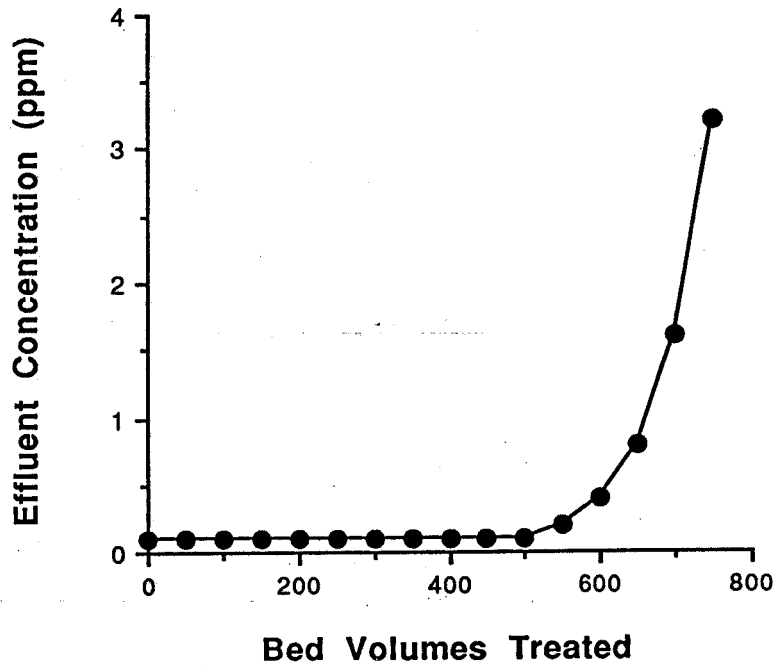
Figure 1.
Typical Breakthrough Curve
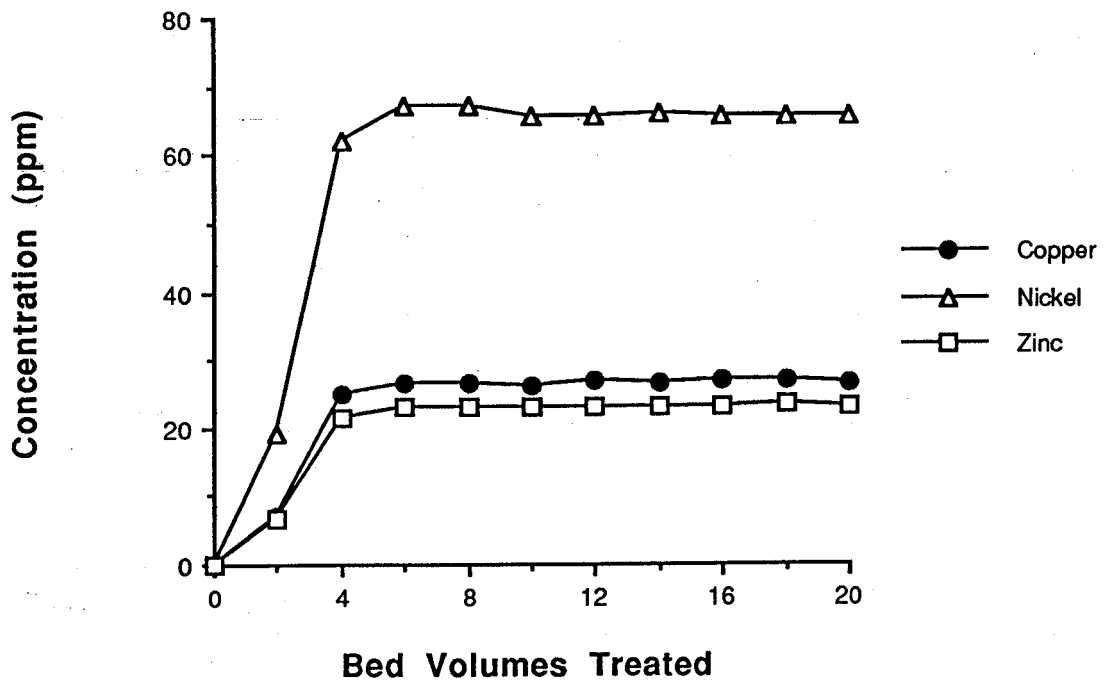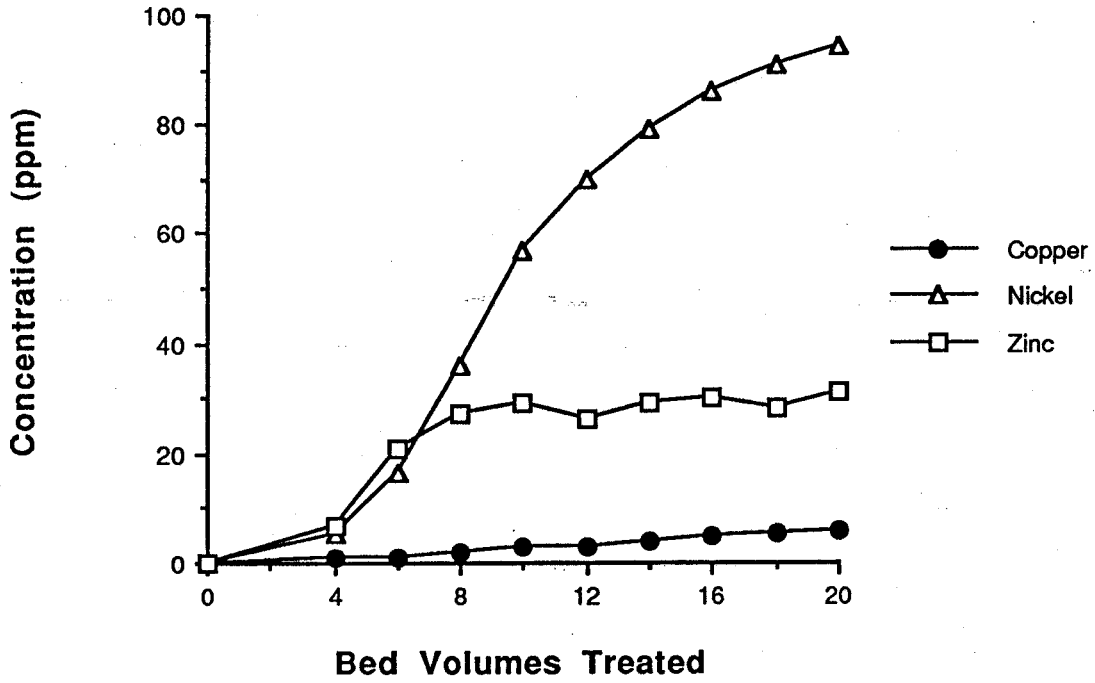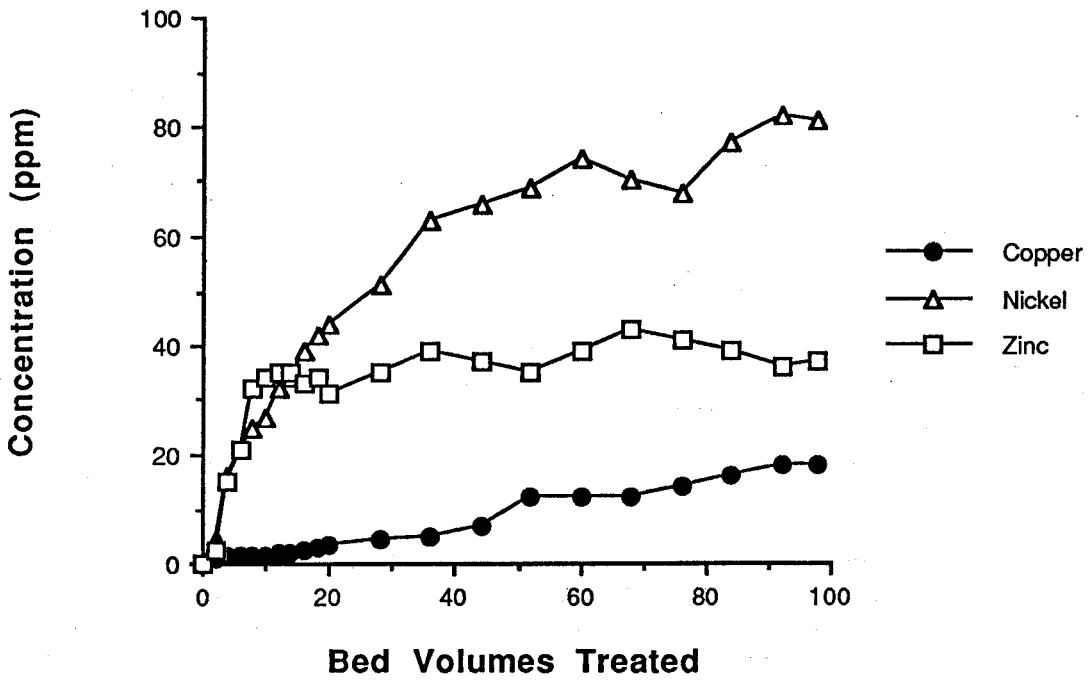

Figure 2. AZ-206.
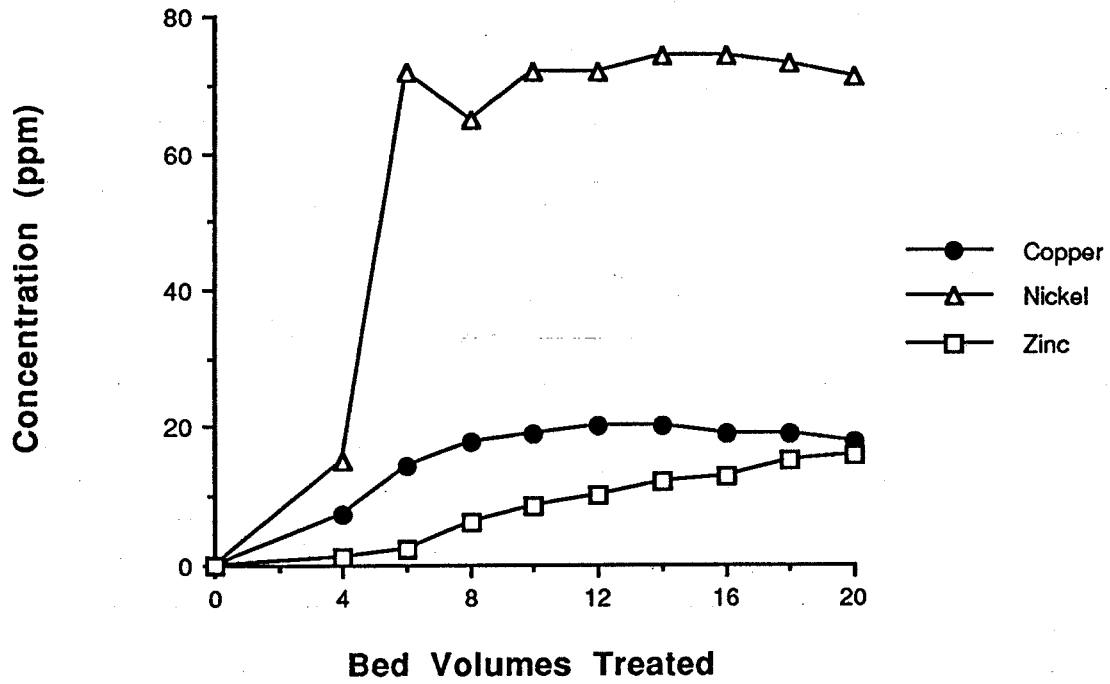
Figure 3. AZ-505

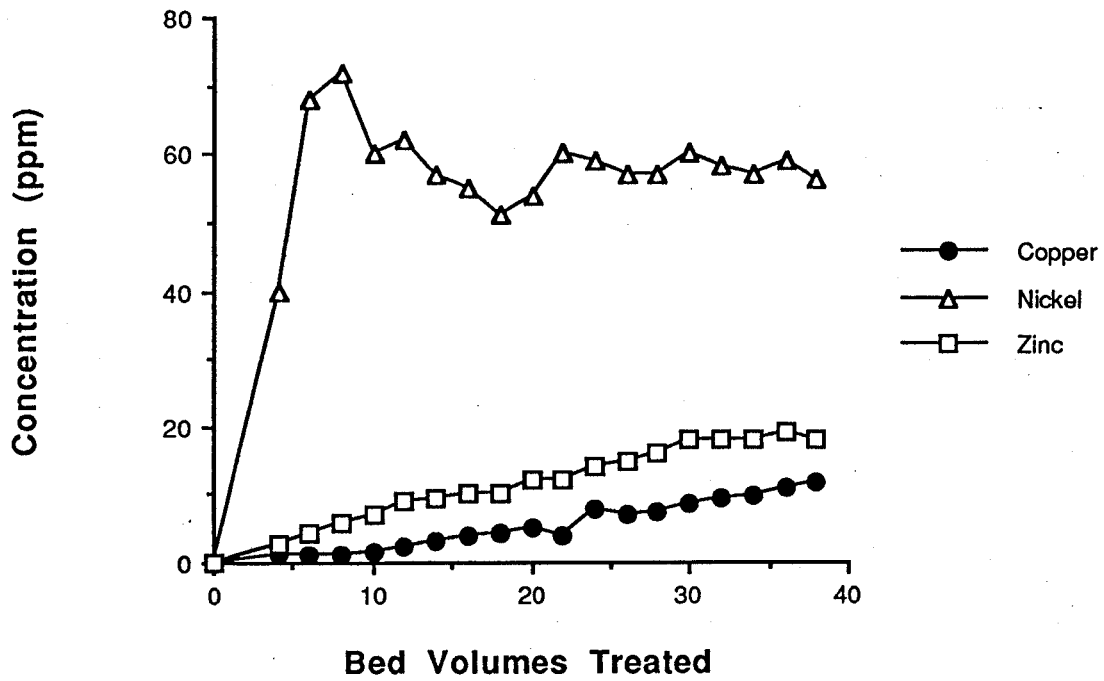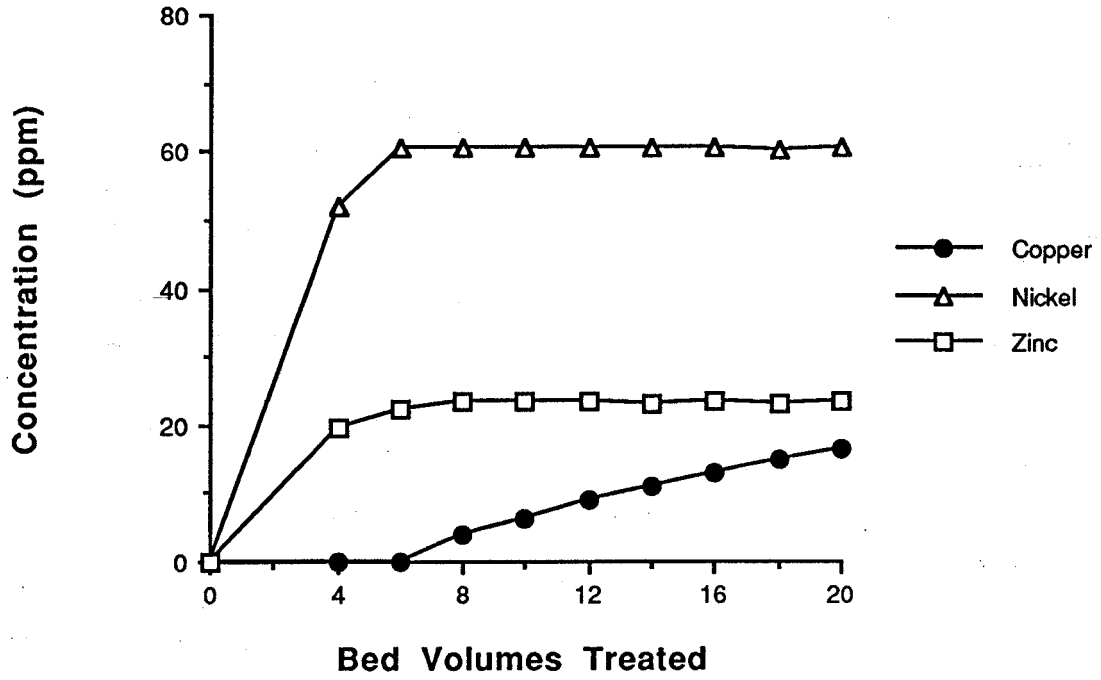Figure 4. AZ-506.

Figure 5. AZ-509.

Figure 6. AZ-511.

Figure 7. AZ-105

- ● Copper
- △ Nickel
- □ Zinc

Concentration (ppm) vs Bed Volumes Treated

Figure 8. AZ-507.

- ● Copper
- △ Nickel
- □ Zinc
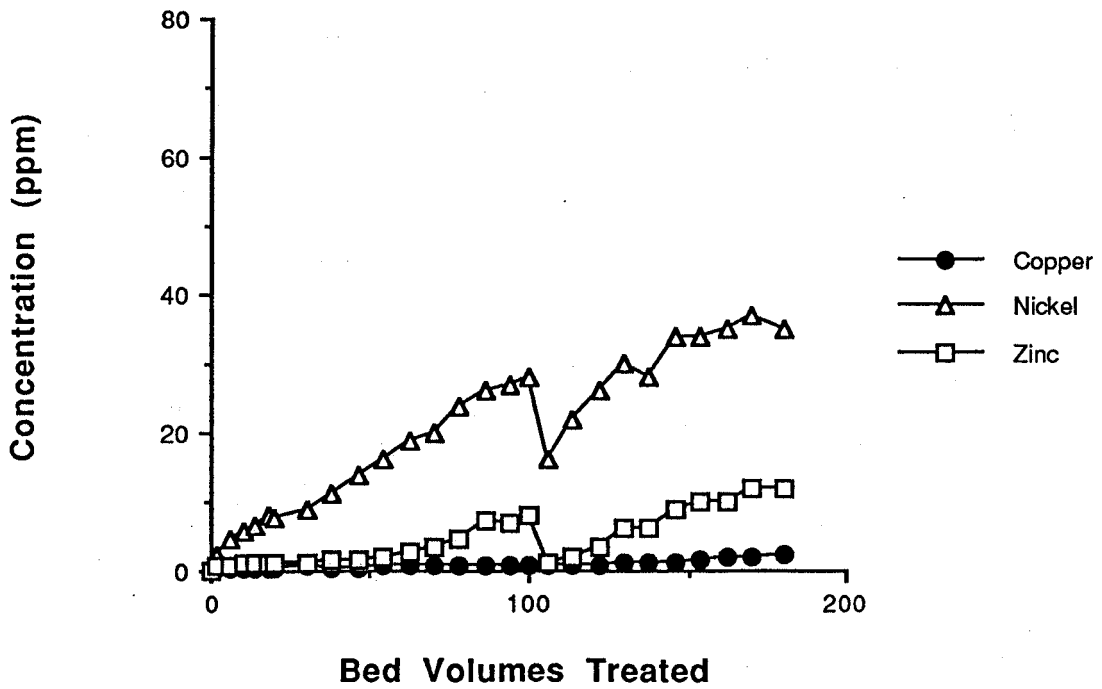
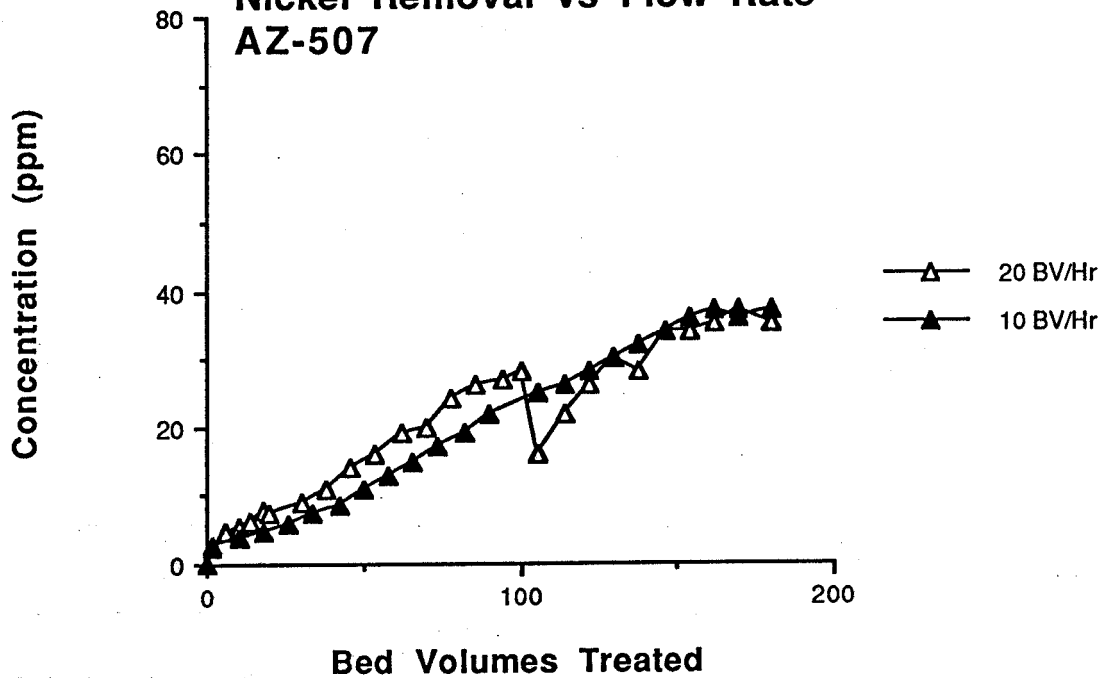Concentration (ppm) vs Bed Volumes Treated

Figure 9.
Nickel Removal vs Flow Rate
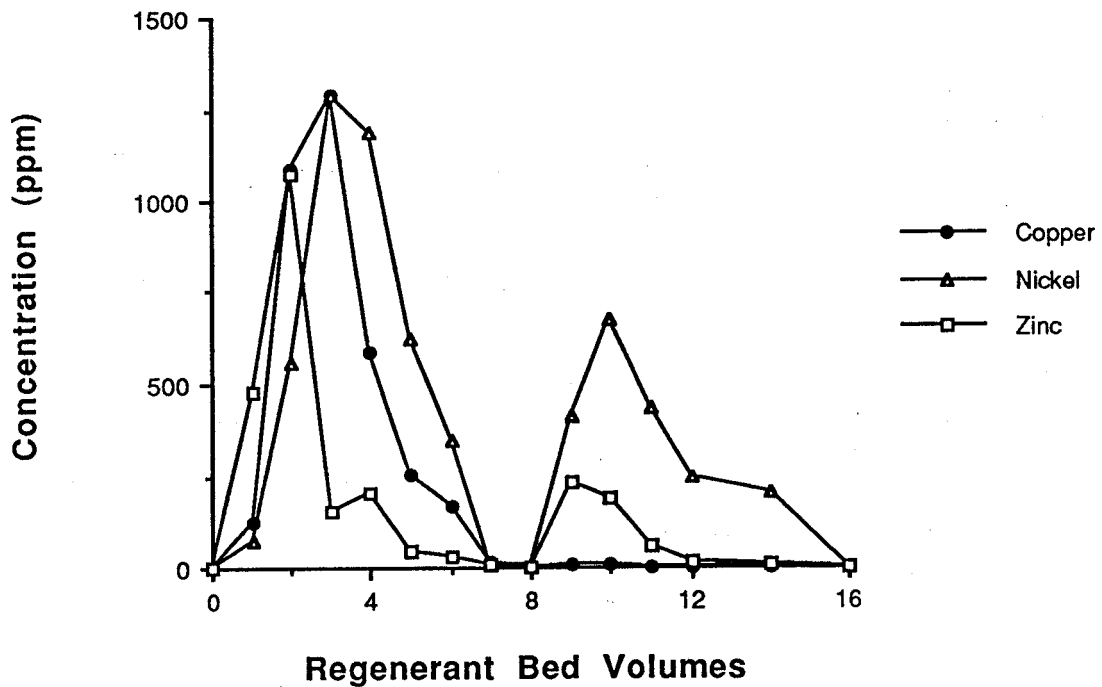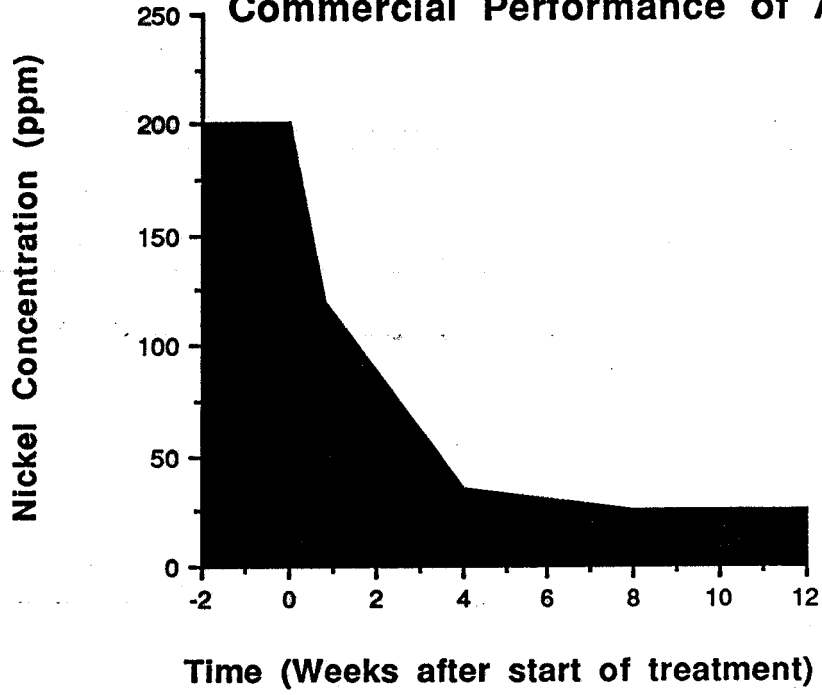AZ-507

Figure 10.
Regeneration of AZ-507

Figure 11.
Commercial Performance of AZ-507

References for "Continuous Purification of Trivalent Chromium Plating Baths."

1.   U.S. EPA, AESF/EPA Symposium, Orlando, FL, Feb., 1989.

2.   H. Gold, et al., <u>Metals Speciation, Separation, and Recovery</u>, edited by J.W. Patterson and R. Passino. 1987, Lewis Publishers, Chelsea, MI.

3.   J.M. Hosea, P.M. Nelis, M.D. Mayne, M.C. Greene, "Metal Recovery by Ion Exchange - Seven Crucial Issues," AESF/EPA Symposium, Miami, FL, Feb., 1990.

4.   Personal communication with various ion exchange resin manufacturers.

5.   B.A. Bolto and L Pawlowski, <u>Wastewater Treatment by Ion Exchange</u>. 1987, E.&F.N. Spon Publisher, New York.